Comments on "Validity of Einstein Relation in Disordered Organic Semiconductors"

Wetzelaer, Koster, and Blom [1] recently concluded that the classic Einstein relation $\frac{D}{\mu} = \frac{kT}{q}$ is still valid in disordered semiconductors in thermal(quasi)equilibrium by studying the diffusion-driven currents of single-carrier diodes. This is in contrast to the previous theoretical prediction [2] and empirical observation [3], where the Einstein relation increases with $1/T$. We will discuss the reason for this discrepancy and suggest that the ideality factor experiment might not be suitable for verifying the Einstein relation in organic semiconductors. A hint for that can be found in [4]. However, due to their use of the MMA model a direct comparison to experiment is not possible [5].

Note that Bolm et al. analyzed their experimental data based on the Shockley diode equation $J = J_0\left[\exp\left(\frac{qV}{\eta kT}\right)-1\right]$, where η is the ideality factor that is related, but not equal,to the Einstein relation. To make our discussion general we will first examine an exponential DOS and then a Gaussian one. Based on the exponential DOS $g(E) = \frac{N_t}{kT_0}\exp\left(\frac{E}{kT_0}\right)$, the carrier concentration, the concentration dependent mobility, and the Einstein relation read respectively as [6]

$$n = n_0 \exp\left(\frac{E_F}{kT_0}\right), \mu = \mu_0 n^{\frac{T_0}{T-1}}, \frac{D}{\mu} = \frac{n}{q\frac{\partial n}{\partial E_F}} = \frac{kT_0}{q}. \tag{1}$$

Here we can see that in disordered organic semiconductors with an exponential DOS, the Einstein relation will deviate from the classic one with pre-factor T_0/T. Based on equations (1), the drift and diffusion current in a diode can be calculated as

$$J = q\left[n\mu\frac{\partial V}{\partial x} + D\frac{\partial n}{\partial x}\right] = q\mu_0\left[n_0^{\frac{T_0}{T}}\frac{dV}{dx} + \underline{\frac{kT}{q}}\cdot\frac{dn_0^{\frac{T_0}{T}}}{dx}\right]. \tag{2}$$

More interestingly, we find that the expression $n^{T_0/T} = \left[n_0\exp\left(\frac{E_F}{kT_0}\right)\right]^{T_0/T} = n_0^{T_0/T}\exp\left(\frac{E_F}{kT}\right)$ has a similar temperature dependence as in the non-degenerate semiconductor. By comparing equation (2) here to equation (3) in [3], it is clear that due to the concentration dependent mobility, the Einstein relation part in the diode equation is the same as that of the classic one and the correct Einstein relation pre-factor T_0/T has been eliminated completely.

Next, we extend the ideality factor model to Gaussian DOS $g(E) = \frac{N_t}{\sqrt{2\pi}\sigma^*}\exp\left(-\frac{\epsilon^2}{2\sigma^{*2}}\right)$(in normalized energy and $\sigma^* = \sigma_0/kT$). In this situation, the carrier concentration $n = \int\frac{g(\epsilon)}{1+\exp(\epsilon-\epsilon_F)}d\epsilon$ and Einstein relation could be calculated as

$$\frac{D}{\mu} = \frac{kT}{q}\frac{\int\frac{\exp\left(-\frac{\epsilon^2}{2\sigma^{*2}}\right)}{1+\exp(1+\exp(\epsilon-\epsilon_F))}d\epsilon}{\int\frac{\exp\left(-\frac{\epsilon^2}{2\sigma^{*2}}+\epsilon-\epsilon_F\right)}{[1+\exp(\epsilon-\epsilon_F)]^2}d\epsilon}. \tag{3}$$

Connecting equation (3) with the drift diffusion equation leads to the current

$$J = \frac{2}{L}\int_0^V \sigma(V,T)\,dV, \tag{4}$$

where L is the diode thickness and σ is the conductivity

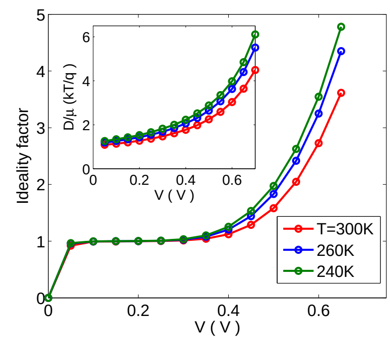

FIG. 1: The computed ideality factor as function of the voltage for different temperature (disorder parameter $\sigma_0 = 0.12$ev). The inset shows the Einstein relation in this situation.

that can be calculated by substituting the Gaussian DOS into equations (4)-(8) in [6]. The ideality factor η can then be derived numerically using $\eta = \left(\frac{kT}{q}\cdot\frac{\partial \log J}{\partial V}\right)^{-1}$. The results are shown in Fig. 1. Here, one can see clearly again, while the Einstein relation could deviate from 1 dramatically, the ideality factor is still weakly temperature dependent and close to 1. Hence we conclude that the temperature independent ideality factor can not be used to prove or disprove the validity of the generalized Einstein relation.

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